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The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

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Abstract

Recently, X-ray absorption spectroscopy (XAS) and related derivative measurements have been used to demonstrate the Pu 5f states are strongly relativistic and have a 5f occupation number near 5. Owing to the success in this regime, it has been argued that the XAS measurements should be a powerful tool to probe 5f occupation variation, both as a function of elemental nature (actinide atomic number) and as a function of physical and chemical perturbation, e.g. oxidation state. It will be shown here that XAS and its related measurements fail in this latter aspect for a wide variety of uranium compounds. Possible causes will be discussed.

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I   Introduction

The nature of the outer electrons in the actinides has been the subject of much investigation, debate, evolving opinion and ongoing controversy. By outer electrons, it is meant the electrons outside of the Radon (Rn)-like core of 86 electrons. Because the term of "valence electrons" is often restricted to the non-f electrons, the more generic expression of "outer electrons" will be used here.

For the neutral Actinides and Rare Earths, the following equations can be used. Z is the atomic number.

Configuration	=	$[\text{Rn-86}]\ 7s^{ns}\ 7p^{np}\ 5f^{nf}\ 6d^{nd}$	Eq 1a
Configuration	=	$[\text{Xe-54}]\ 6s^{ns}\ 6p^{np}\ 4f^{nf}\ 5d^{nd}$	Eq 1b
Occupation-Act	=	$n_{outer} = n_s + n_p + n_f + n_d\ =\ Z - 86$	Eq 2a
Occupation-RE	=	$n_{outer} = n_s + n_p + n_f + n_d\ =\ Z - 54$	Eq 2b

For U (Z = 92), $n^U_{outer} = 6$ and for Pu (Z = 94), $n^{Pu}_{outer} = 8$.

Initially, it was argued that the actinides were a 6d series [1], based upon physical data such as atomic volume trends as a function of Z. (Figure 1, Ref. 2) Subsequently, it was shown that the atomic volume and bulk modulus effects could be explained in terms of 5f behavior. [3] It is now generally accepted that the actinide elements are "trivalent," i.e. $n_s + n_p + n_d = 3$ and that 5f occupation (n_f) varies linearly with Z [4], although there is not complete unanimity in this view [5]. Based in part upon the success of the Russell-Saunders-coupling-models for the 4f states in the Rare Earths [6, 7], this picture was applied to the actinides. Using X-ray absorption spectroscopy (XAS) and related measurements of the transitions

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between the 5d and 5f states and between the 4d and 5f states [9-13], it was shown that the Russell-Saunders model fails for Pu and that the 5f occupation of Pu must be near 5. ($n^{Pu}_{5f} \approx 5$) Later, hard X-ray measurements confirmed and refined these results for Pu [14]. The essence of the 4d XAS and 5d XAS is illustrated in Figure 2. The reduction in the $4d_{3/2}$ intensity in Pu versus that in U and the disappearance of the pre-peak in Pu are due to the jj-skewed intermediate coupling model for the Pu 5f states [9-12]. In fact, to a first approximation level, it is possible to think of the states in a pure jj-limiting-case-model. Extension of the related measurements, Electron Energy Loss (EELS), further across the series, has confirmed the validity of the Pu results and interpretation [16-18].

After the success of this approach as a function of Z or elemental nature [9-12, 16-18], it was proposed that the analytical method could be used to follow changes in the 5f occupation as a function of oxidation state [19]. It was argued that by changing the oxidation state, the 5f occupation would change and that these changes in 5f population would manifest themselves in the XAS and related measurements. Unfortunately, there is an older body of literature that indicates otherwise. In 1987, Kalkowski, Kaindl, Brewer and Krone [20] carried out an extensive XAS study of a wide variety of uranium compounds. These include uranium metal, uranium intermetallics, UO_2, UF_4 and UO_3. As shown in their Figure 8, the 5d XAS data of these materials seem to be essentially invariant. A subset of these spectra is included in the rightmost panel of Figure 3 in this paper.

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As can be seen there, the 5d XAS spectra of the α-U, UF_4, UO_2, and UO_3 are very similar, with only slight changes. This is despite very significant changes in oxidation state and 5f occupancy, as confirmed by the corresponding X-ray photoelectron spectroscopy (XPS) data of α-U, UF_4, UO_2, and UO_3, in the two middle panels of Figure 3. (Except for the UF_4, all of the XPS data in Figure 3 are from Veal and coworkers [21-24]. The UF_4 XPS data are from Thibaut et al. [25], with confirmation by Teterin and coworkers [26,27].) In terms of formal charge and electron configuration, these materials range from neutral and $5f^3(spd)^3$ for α-U; through 4+ and $5f^2(spd)^0$ for UF_4 and UO_2; to 6+ and $5f^0(spd)^0$ and UO_3 and UF_2O_2, as demarked in the leftmost panels of Figure 3. Of course, formal charge is an extreme limit, assuming complete ionization, but it does provide a useful tool for keeping track of oxidation effects. Moreover, the XPS spectral results are consistent and well understood [4, 21-27]. In the metallic α-U, the triangular peak with the sharp edge at the Fermi Energy is associated with the three delocalized 5f electrons. In UF_4 and UO_2, the narrower feature near the Fermi Energy is assigned as the 5f peak and the broader peak at larger binding energy is interpreted as the 2p derived states, either F2p or O2p. The UF_4 features are shifted to larger binding energies, as would be expected for the stronger oxidant, F, versus the weaker oxidant, O. For the UF_2O_2, and UO_3, the 5f peak near the Fermi energy is now completely gone, leaving only the broad 2p feature dominating the spectra. The systematics of this progressive oxidation as a

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function of oxidation concentration have been convincingly investigated in detail, including UO_2, U_4O_9, U_3O_8, and UO_3 [4, 21-24].

The U4d XAS data confirm the trends observed in the U5d XAS. As can be seen in the left panel of Figure 4, the U4d XAS spectra of UF_4 (4+, $5f^2(spd)^0$) and of α-U (neutral, $5f^3(spd)^3$) are essentially identical. The peak ratios reported by KKBK [20] are the same for both: $I_{5/2}/I_{3/2}$ = 2.1. This corresponds to a Branching Ratio (BR) of 0.68, using BR = $I_{5/2}/(I_{5/2} + I_{3/2})$. (For a discussion of the error analysis of peak area determinations and limits on significant digits, please see Appendix 1 below.) At this point it is useful to ask whether a change of 5f occupation by a single unit can result in an observable change in the 4d XAS spectra. As shown in the right panel of Figure 4, in going from Pu (n_f = 5) to AmH_2 (n_f =6) [11], there is a real and significant reduction in the $4d_{3/2}$ (N_4) peak intensity. (The 4d XAS of Am and AmH2 are essentially the same, with a branching ratios of 0.93 for each [11, 16, 17]. Again, an absence of chemical sensitivity.) Thus, the absence of an intensity variation between U and UF_4 is troubling.

Furthermore, one can ask the analogous question about the 5d XAS data in Figure 3: Are there changes in the 5d XAS spectra as the atomic number and 5f occupation change? Of course, the answer is yes, as illustrated in Figure 5. Here, the 5d XAS spectra of α-U (n_f = 3), UF_4/UO_2 (n_f =2) and UO_3 (n_f = 0) are directly compered to EELS data of AmH_2 (n_f = 6), Pu (n_f = 5) and α-U (n_f = 3), so the series is n*, n*-1 and n*-3. The changes for the uranium materials are much smaller

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than those for the elemental series. (Please also note that the 5d EELS of α-Pu and δ-Pu(Ga) in Figure 5 are essentially the same, as well as the 4d EELS of α'-Pu(Ga) and δ-Pu(Ga) in Figure 4. [11] Again, an absence of chemical sensitivity, albeit one of possibly lessened significance, being merely between phases.) A detailed discussion of the underlying reasons for the changes for Pu and Am is provided in Reference 11.

Thus, it is clear that the 4d XAS and 5d XAS of the uranium compounds are largely invariant and insensitive to changes in oxidation state and 5f population, despite marked and well-understood variations in the XPS of these same materials. Before going on to a discussion of potential causes, it is necessary to digress to a discussion of the techniques and the underlying physics, including a consideration of Rare Earth (4f) results for comparison with the observations of actinide (5f) behavior.

II   Experimental

Some of the relevant spectroscopic processes are shown in Figure 6. XPS can sample the occupied density of states (ODOS) or Valence Bands (VB). XAS and Bremstrahung Isochromat Spectroscopy (BIS) sample the unoccupied density of states (UDOS) or Conduction Bands (CB). BIS is the high energy variant of Inverse Photoelectron Spectroscopy (IPES). In all of these processes of photon absorption and emission, there is great selectivity derived from the electric dipole transitions with $\Delta l = +/- 1$. We will return to these issues below.

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Details of each specific experiment can be found in source article, as referenced in the text.

III   Spectral Results and Discussion

IIIa   Rare Earths and the case of Ce XAS

It is useful to consider the case of the X-ray Absorption of Ce, using the corresponding 3d and 4d thresholds [29], as shown in Figure 7. First, it should be noted that the Ce 4d XAS exhibits prepeak structure, below the "giant resonance" near 120 eV. This was first explained by Dehmer, Starace, Fano, Sugar and Cooper in 1971[28]. The pre-peaks arise because of the combination of (1) angular momentum coupling, between a core hole and the partially filled f states, and (2) coulombic repulsion between the electrons [9,11, 28]. The magnitude of the impact of the electron repulsion depends upon the nature of the angular momentum coupling. This is the underlying physics causing the wide dispersion of the pre-peaks in Figure 7. The effect is well understood, as evidenced by the strong agreement between the 4d calculated results in Figure 7 with the experimental XAS and EELS data [29]. The X-ray absorption event is described in Eq 3.

$$d^{10}f^{nf} + h\nu \rightarrow d^9f^{nf+1} \hspace{4cm} \text{Eq 3}$$

For Ce, $n_f = 1$, so $n_f + 1 = 2$. Thus, both the 4d and 4f manifolds are partially occupied and angular momentum coupling between the d and f manifolds can occur. It is known that when one reaches the end of the Lanthanide Series, the pre-peaks can disappear [9,11,30]. This is because, if $n_f = 9$, then $n_f + 1 = 10$, and there will be a filled f manifold, unable to couple with the hole in the d-states.

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At this point, it is beneficial to attempt to quantify the magnitudes of the spin-orbit-splittings in the RE 4f and actinide 5f states. Because of the combination of the angular momentum coupling and coulombic repulsion, it is often difficult to get at the spin-orbit splitting directly. For example, consider the summary in Table 1. This has been compiled from the publications of Baer, Lang and Cox [7, 31, 32], that utilized XPS and Bremstrahlung Isochromat Spectroscopy (BIS) to probe the occupied and unoccupied sites, respectively. Note that often the XPS results are described as having multiple peaks. The BIS peak structure is simpler but broader, suggesting unresolved multiplets beneath the single and double peaks. However, as the f levels approach being filled (n_f =14) or half-filled (n_f = 7), the spectra simplify, giving rise to simpler spectra. The effect is so strong that Eu and Yb are divalent, with $(spd)^2$. This divalency is also manifested in the atomic volumes in Figure 1. Qualitatively, the half-filling of the RE 4f bands is strikingly different than the filling of the Pu and Am $5f_{5/2}$ sub-band [9,11]. The "magic" number for Eu and Gd is 7. (The underlying stabilization has a magnetic component here, with an orbital quenching and spin alignment.) The "magic" number for Pu and Am is 6. Seven is the hallmark of nearing the Russell-Saunders coupling limit. Six is the manifestation of being near the jj coupling limit. Thus, qualitatively, the RE 4f states are near the Russell-Saunders limit and the 5f states are near the jj coupling limit, but before continuing with this discussion, let us now return to the quantitative evaluation.

Because of the n_f =14 configurations in Yb and Lu, the separation between peaks in the spin-orbit split doublets can be used to extract the spin-orbit splitting.

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(With the filling of the 4f manifold, the behavior simplifies, interactions diminish and merely the spin-orbit spilt doublet is observed.) This process can be extended to higher Z. From fundamental atomic physics, it is known that the spin-orbit splitting should scale with Z^4 [33]. Thus, using the 4f binding energies from Reference 34, one can generate the results in Figure 8. Taking the quartic root of the experimental values and extrapolating linearly to lower Z, it is possible to generate spin-orbit splitting values for the entire Lanthanide series. The success of the least squares fit upon the experimental quartic roots confirms the Z^4 dependence. Moreover, it is clear that the energy separation of the $4f_{7/2}$ and $4f_{5/2}$ peaks is on the scale of 1 eV or substantially less, throughout the actinide series. Because there may be some f-f shielding of the Z changes, one might expect that the reduction in spin-orbit splitting may be lessened, with the values hovering between ½ and 1 eV.   An experimental confirmation of these estimates is given in the inset in Figure 8. Here, Fano Spectroscopy [35-37] has been performed upon a Ce sample. Fano Spectroscopy is a variant of spin-resolved photoelectron spectroscopy, where a chiral excitation is used. The chiral excitation can be either circularly polarized photons or an unpolarized source in a chiral experimental configuration. The different spins provide a way to look at the two possible components within a spin-orbit split pair.   As can be seen in the inset, the splitting between the spin up and spin down features is of the scale of ½ eV or less, confirming the estimates from above.

As a counter balance to the RS behavior on the RE 4f states, consider the result shown in Figure 9. In the top panel of Figure 9 is the experimental result of

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Baer and Lang [38], using BIS to probe the unoccupied electronic structure of uranium. In the lower panel is an estimate of the unoccupied density of states, from Kutepov et al [10, 39-41]. The two main features, the peak near 2/3 eV and the broad peak near 2 eV, are associated with the $5f_{5/2}$ and $5f_{7/2}$ manifolds, respectively. Thus the U5f spin orbit splitting is on the order of 4/3 eV. This is significantly greater than our estimate of ½ to 1 eV for the Rare Earths.

Thus, it is possible to think of the Ce behavior in particular, and the Rare Earths with partially occupied 4f states in general, in terms of the Russell-Saunders or LS limit, as illustrated in the cartoon in Figure 10. In this case, the separation of the $f_{7/2}$ and $f_{5/2}$ manifolds is small enough to render it unimportant and no $f_{5/2}$ substructure filling is observed. However, for Pu and Am, with $n_f = 5$ and $n_f = 6$ respectively, the impact of the filling of the $5f_{5/2}$ manifold is obvious. As shown in Figure 5, the pre-peak disappears for Pu and one of the two parts of the "giant resonance" is eliminated or at least reduced in the AmH_2. This second effect, the loss of intensity in the $5d_{3/2}$ peak, is a related but slightly different event than the loss of the pre-peak. This same effect can be seen in Figure 4, with the reduction of the $4d_{3/2}$ (N_4) peak in Pu and the near elimination of the $4d_{3/2}$ (N_4) peak in AmH_2. The loss or reduction of the $4d_{3/2}$ (N_4) peaks is driven by the electric dipole selection rules with a $d_{3/2}$ to $f_{7/2}$ transition being forbidden or at least strongly repressed, and the filling of the $5f_{5/2}$ manifold. For the sake of comparison, note the strength of the Ce $3d_{3/2}$ peaks in Figure 7. The mixing of the $4f_{5/2}$ and $4f_{7/2}$ manifolds in the LS limiting case lessens, if not completely negates, the possibility of the manifestation of the

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forbidding of the $d_{3/2}$ to $f_{7/2}$ transition.

Finally, one last aspect of the Ce and actinide spectra should be described. The lifetime broadening in the actinides is significantly greater than that in the Rare Earths. This can be seen in Figures 1, 4 and 7. The fine structure in the Ce 3d XAS can not be observed in the 4d XAS of U, Pu or Am.

IV   Discussion

Let us briefly summarize the experimental results for the 4d and 5d XAS of uranium compounds. For the 5d XAS in Figure 3, there are three main features: (1) the prepeak near 100 eV, denoted with two blue lines; (2) an initial rise, near 108 eV, denoted with another pair of blue lines; and second rise and overall peaking, with three blue lines, near 115 eV. The assignments are as follows: (1) with a prepeak origin similar to that in Ce; (2) with the $5d_{5/2}$ (O_5) transition; and (3) with the $5d_{3/2}$ (O_4) transition. While there are inklings of changing multiplet structure underlying these features, the variations are small. (Please see the blue lines.) This loss of detail is directly attributable to the large lifetime broadenings that are intrinsic to these d-f transitions. Thus the only large changes are events such as the loss of the prepeak or the loss of the $5d_{3/2}$ (O_4) transition with near filling or complete filling of the $5f_{5/2}$ sub-band. For the 4d XAS, the lifetime broadening is so severe that there is a complete loss of the kind of fine structure seen in the Ce 3dXAS, rendering the peak intensity variations as the only measurable quantity. Moreover, as can be seen in Figure 4, the peak ratios are the same for U metal and UF_4.

The manifestation of strongly relativistic effects in the XAS of Pu and Am is

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scientifically intriguing and real [9-12]. Moreover, there is no doubt that this larger spin-orbit splitting will underlie the electronic structure of the actinides [11, 41]. However, it manifestations may be significantly abated or complicated by the application of other forces or potentials. For Pu, other effects, such as the crystal field splitting of the 5f states, seem to be unimportant. The 4d XAS spectra of α-Pu, δ-Pu(Ga), oxidized Pu and radiation damaged Pu are all the same [10,19]. There are small changes in the 4d XAS between different forms [19], but it is not clear that the reported variations are statistically meaningful. (See Appendix I.)[10] Perhaps, this is a result of the contraction of the Pu5f electrons inside the valence (spd) electrons, covalency, or the nearly filled nature of the $5f_{5/2}$ manifold with n_f =5. However, for the uranium compounds, none of these factors should apply. It is commonly agreed the uranium metal has a significant degree of delocalization, ruling out the contraction argument. While there is certainly a covalency in OU_2 [42], both the UF_4 and UO_2 show the same result. Finally, at $n_f \approx 3$, there is no near-filling of any jj substructure.

Instead, it seems likely that crystal field splitting may be playing a key role. The lower the symmetry, the greater the mixing will be. Thus, let us consider a high symmetry case, with minimal mixing. With that in mind, the case of octahedral double groups will be discussed. Shown in Figure 11 is a diagram based upon the single f-electron ($5f^1$) calculations performed by Edelstein et al [43] and Lukens [44], and similar to the single f-hole ($5f^{13}$) picture of Burns and Axe [45]. The important point here is that the application of even a highly symmetric crystal field will split the 5f states, wrecking the 6-fold degeneracy of the j = 5/2 manifold and the 8-fold

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degeneracy of the j = 7/2 manifold. In the spherically symmetric, atomic models [8,10-12, 16-19], the mixing can be generated by utilizing an intermediate state model, with elements of both Russell-Saunders and jj behavior. Perhaps a more fundamental mixing is produced by the application of crystal field, breaking degeneracies and mixing states from the j = 3/2 and j = 5/2 manifolds. Unfortunately, despite their sophistication in terms of the treatment of angular momentum coupling and coulombic repulsion, the atomic models do not provide a mechanism for including the reductions in symmetry associated with crystal field splitting. It would be of great use to recalculate the 5f states under a large spin orbit splitting and a significant crystal field and then calculate the electronic transitions and branching ratios with the same degree of quality as the atomic calculations. Perhaps the degree of mixing in the 5f states of U materials is sufficient to render the 4d BR's and the 5d spectra invariant with changes in 5f occupation.

V   Conclusions

The absence of chemical sensitivity in the 4d and 5d XAS of uranium compounds has been described. Experimental limitations and one possible cause, crystal filed splitting, has been discussed.

VI   Acknowledgements

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VII   Appendix: Peak Fitting, Error Analysis and Significant Digits

VIIa   Error Propagation in Peak Fitting

Let us consider the simplest possible case of error propagation in a peak fitting: a triangular function sitting on a noisy background. (This assumes that we know the peak shape perfectly, which is usually an inaccurate assumption. However, let's consider this rather optimistic scenario.) The triangular peak has a height h, base b and angles of ϑ_1 and ϑ_2 between the sides of the triangle and its base. By differentiating, it is possible to get the error estimates. The noisy background will cause an uncertainty in the determination of the height of the triangle, Δh. This will propagate into the error in the areal determination.

Area   = A   = ½ bh = $h^2[(1/\tan\vartheta_1) + (1/\tan\vartheta_2)]/2$ Eq A1

ΔA = $h[(1/\tan\vartheta_1) + (1/\tan\vartheta_2)]\Delta h$ Eq A2

$\Delta A/A$ = $2\Delta h/h$ Eq A3

The data will have some obvious signal to noise: S/N. For our purposes we will use N/S.   If we set S equal to h, then the scatter in the background will be N. We can see the noise by simply looking at the spectra. For a fairly good spectrum, it is common to see S/N = 50 and N/S = 0.02 or 2%.

We can improve our estimate of the position of the baseline and lower Δh by using multiple points on either side of the peak. In essence, we will calculate a standard deviation (SD) of the scatter, with n_p = number of points.

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$$SD = [\Sigma_{i=1}^{i=n} \{X_i - X_{ave}\}^2/(n_p-1)]^{1/2} \qquad \text{Eq A4}$$

If the noisy data were sinusoidal, then we could estimate the SD, by integrating over one period or more. The peak-peak value would be N.

$$SD = (N/2)\left[\int_{\phi=0}^{\phi=2\pi} \sin^2\phi \, d\phi \Big/ 2\pi\right]^{1/2} = (N/(2\sqrt{2}) \approx 0.35N$$

$$\text{Eq A5}$$

As one might expect, the statistical estimate of the error associated with the noise should be less that the peak-to-peak value. It seems reasonable that SD equals about N/3. We can use that estimate in our error calculation. We'll also use S as h.

Going back to the percentage uncertainty in the height determination, we get

$$\Delta h/h = SD/h \approx (N/3)/S = (1/3)(N/S) \qquad \text{Eq A6}$$

And

$$\Delta A/A = 2\Delta h/h \approx (2/3)(N/S) \qquad \text{Eq A7}$$

And

$$(\Delta A/A)/(N/S) \approx 2/3 \qquad \text{Eq A7}$$

So, if the N/S ≈ 1/50 and then ΔA/A ≈ 2/150 = 1.3%. Of course, this is an optimistic evaluation. If the peak shape is unknown or the background has irregularities, the error would increase substantially. Thus, it is probably wise to use 1%, as an estimate of the minimum error.

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VIIb   Error Propagation in the Branching Ratio Analysis

There are three ways that we can express the relative intensities of the $d_{5/2}$ and $d_{3/2}$ peaks. These are shown on Eq B1, B2 and B3 below. A is the peak area.

R $=$ $A_{3/2}/A_{5/2}$ ≤ 1 Typically   Eq B1

R' $=$ $A_{5/2}/A_{3/2}$ $=$ $1/R$ ≥ 1 Typically   Eq B2

BR $=$ $A_{5/2}/(A_{5/2} + A_{3/2})$ $=$ $1/(1 + R)$ Branching Ratio   Eq B3

We've included R' because that is how KKBK [20] report their results.

We can get error propagation by differentiating the equations above and taking the absolute values. EEP is the experimental error percentage.

EEP $=$ $\Delta R/R$ $=$ $\Delta R'/R'$ $=$ $|\Delta A_{3/2}/A_{3/2}| + |\Delta A_{5/2}/A_{5/2}|$ Eq B4

Based upon the discussion in Section VIIa above, we will assume the following.

$|\Delta A_{5/2}/A_{5/2}| = 0.01$ Eq B5

Throughout the data collection, the $4d_{5/2}$ peak remains strong and the usual statistics should apply. However, the $4d_{3/2}$ peak will diminish significantly. With that in mind, let us assume that $|\Delta A_{3/2}| \approx |\Delta A_{5/2}|$. Then, we get the following relations.

$|\Delta A_{3/2}/A_{3/2}| = |\Delta A_{5/2}/RA_{5/2}| = 0.01/R$ Eq B6

EEP $=$ $0.01\{1 + (1/R)\}$ Eq B7

Using these relations, we get the results shown in Table 2. As the $4d_{3/2}$ peak diminishes in intensity, the relative error becomes larger. For the range of interest, i.e. for U, Pu and Am, the error in ΔBR becomes almost 0.01. As discussed in Section VIIa above, this is a very conservative error estimate. Thus, a reasonable minimal error estimate for all BR values should be 0.01.

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Regarding Eq B4 and B7, we could add in quadrature and take the square root instead, reducing the error estimates slightly. However, in the end, for the U, Pu and Am cases, the reasonable minimal error would still be 0.01.

VIIc   Error Propagation in the prediction of n_f

As an estimate of the error in the determination of n_f, let us use the equation for the jj limit from Reference 10. Again, we will differentiate.

BR   =   3/5   + $8n_f/15(14-n_f)$ for $0 \leq n_f \leq 6$ Eq C1

Δn_f = $(14 - n_f)^2(15/112)\Delta BR$ Eq C2

Using $0 \leq n_f \leq 6$ we get the following.

$26\Delta BR$ $\geq$ Δn_f $\geq$ $8.6\Delta BR$ Eq C3

If $\Delta BR \approx 0.01$, then the result below is obtained.

0.3 $\geq$ Δn_f $\geq$ 0.1   Eq C4

This is sufficient for our purposes.

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Table 1

Z (El.)	Config	Occ 4f's XPS	Unocc 4f's BIS	Z (El.)	Config	Occ 4f's XPS	Unocc 4f's BIS
57 (La)	$4f^0(spd)^3$	---	Single				
58 (Ce)	$4f^1(spd)^3$	Weak	Double	65 (Tb)	$4f^8(spd)^3$	Multiple	Double
59 (Pr)	$4f^2(spd)^3$	Single	Double	66 (Dy)	$4f^9(spd)^3$	Multiple	Double
60 (Nd)	$4f^3(spd)^3$	Single	Double	67 (Ho)	$4f^{10}(spd)^3$	Multiple	Single
61 (Pm)	$4f^4(spd)^3$	Radioactive No data		68 (Er)	$4f^{11}(spd)^3$	Multiple	Single
62 (Sm)	$4f^5(spd)^3$	Multiple	Double	69 (Tm)	$4f^{12}(spd)^3$	Multiple	Single
63 (Eu)	$4f^7(spd)^2$	Single	Broad	70 (Yb)	$4f^{14}(spd)^2$	so Doublet	---
64 (Gd)	$4f^7(spd)^3$	Single	Single	71 (Lu)	$4f^{14}(spd)^3$	so Doublet	---

Table 1 Caption
This is a summary of the XPS and BIS data for the Rare Earths from PA Cox, JK Lang, and Y Baer [31,32]. The configurations and further data are available from Reference 7.

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Table 2

| Element	R	EEP	R'=1/R	BR = 1/(1+R)	$R/(1+R)^2$	$\Delta BR = EEP\{R/(1+R)^2\}$
	1.0	.020	1.00	0.50	0.25	0.005
	0.9	.021	1.11	0.53	0.25	0.005
	0.8	.0225	1.25	0.56	0.25	0.006
	0.7	.024	1.43	0.59	0.24	0.006
	0.6	.027	1.66	0.625	0.23	0.006
U	0.5	.030	2.00	0.667	0.22	0.007
	0.4	.035	2.50	0.714	0.20	0.007
	0.3	.043	3.33	0.769	0.177	0.008
Pu	0.2	.060	5.00	0.833	0.139	0.008
Am	0.1	.110	10.00	0.909	0.083	0.009
	0	∞	∞	1	0	---

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Figure Captions

Figure 1 Quoting Ref 2: "Atomic volumes of the 3*d*, 4*f*, and 5*f* elements as a function of the electron count, increasing to the right. Note the parabolic shape of the 3*d* series, the almost constant values of the rare earths Eu and Yb are divalent as metals and have a much larger volume than the other trivalent metals, and the unusual behavior of the 5*f* elements, with a minimum volume near Pu, and a very large increase between Pu and Am."

Figure 2 XAS of the 4d and 5d levels of Pu and U. See text for details. The data are from References 9-13.

Figure 3 Here is a comparison of the Formal charge, valence configuration, XPS and 5d XAS of α-U, UO_2, UF_4, UO_3 and UF_2O_2. E_F is the Fermi Energy. See text for details. The XAS data are from Kalkowski, Kaindl, Brewer and Krone [20]. Except for the UF_4, all of the XPS data are from Veal and coworkers [21-24]. The UF_4 XPS data are from Thibaut et al. [25], with confirmation by Teterin and coworkers [26,27].

Figure 4 Shown here is a comparison of the 4d XAS of α-U, UF_4, α'-Pu, δ-Pu and AmH_2. See text for details. The α-U and UF_4 XAS data are from Kalkowski, Kaindl, Brewer and Krone [20]. The EELS data are from Reference 11.

Figure 5 Shown here is a comparison of the 5d XAS of α-U, UO_2, UF_4, UO_3, α-

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Pu, δ-Pu and AmH$_2$. See text for details. The α-U, UO$_2$, UF$_4$, and UO$_3$

XAS data are from Kalkowski, Kaindl, Brewer and Krone [20]. The

EELS data are from Reference 11.

Figure 6   Spectroscopic processes are shown here. See text for details.

Figure 7   XAS of the Ce 3d and 4d levels, including the corresponding Electron

Energy Loss (EELS) spectra and theoretical simulation of the spectra

(CALC), performed by G. van der Laan [29].

Figure 8   The spin orbit splitting in the RE's is shown here. See text for details.

The spectral data in the inset is from Reference 35.

Figure 9   Unoccupied Density of States of U. Top panel: Experimental result is

from Bremstrahlung Isochromat Spectroscopy (BIS) by Baer and Lang

[38]. Bottom panel: Theory with occupied (neg energies) and

unoccupied (pos energies) 5f Density of States U calculated by A.L.

Kutepov [10, 39-41]. See text for details.

Figure 10 LS and jj limiting cases for transitions between the d core levels and

near valence f states. This assumes electric dipole selection rules.

See text for details.

Figure 11 Octahedral double group states for a single f electron. Following

References 43, 44 and 45. The degeneracies are shown in red boxes.

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds
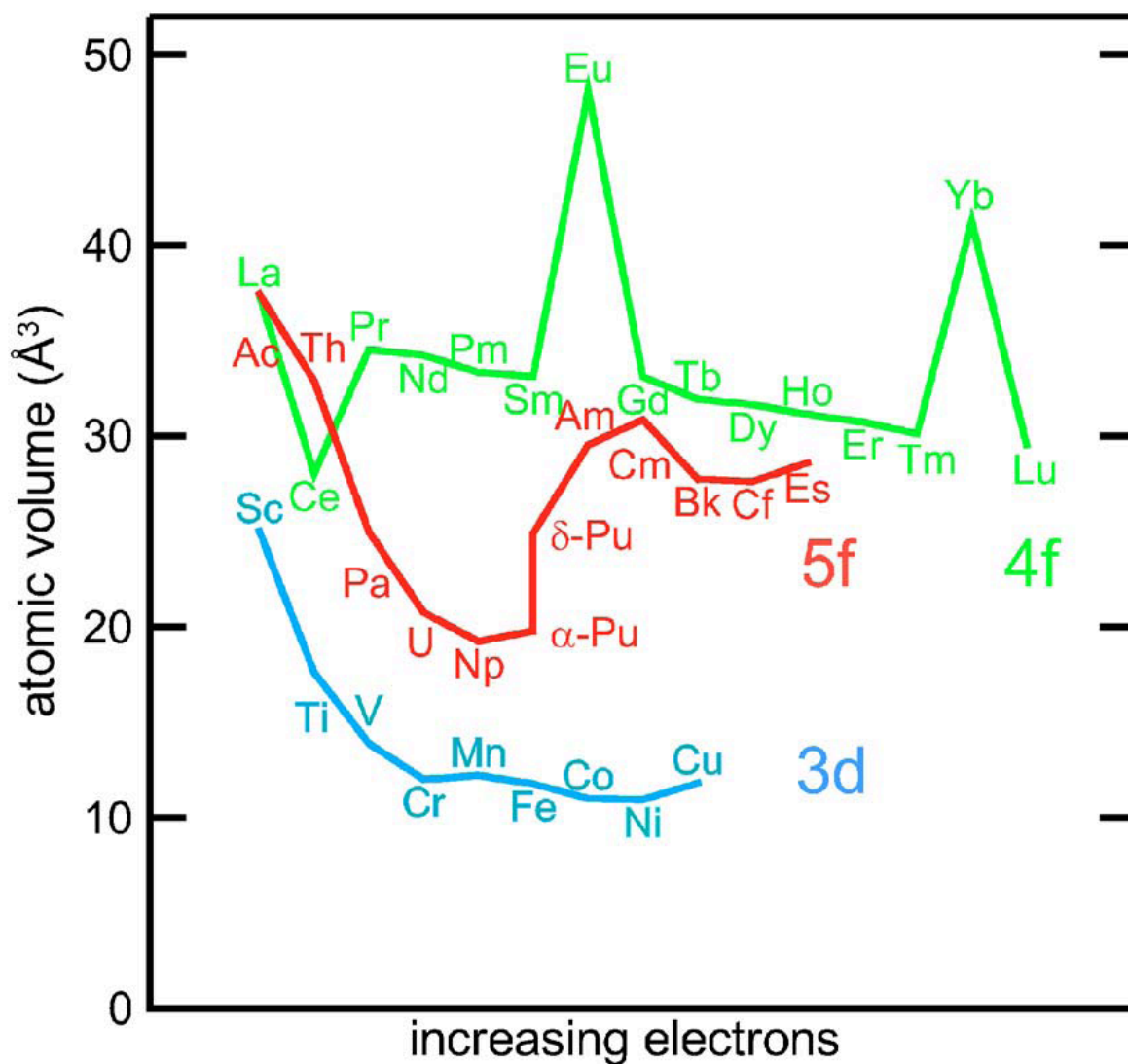
Figure 1

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds
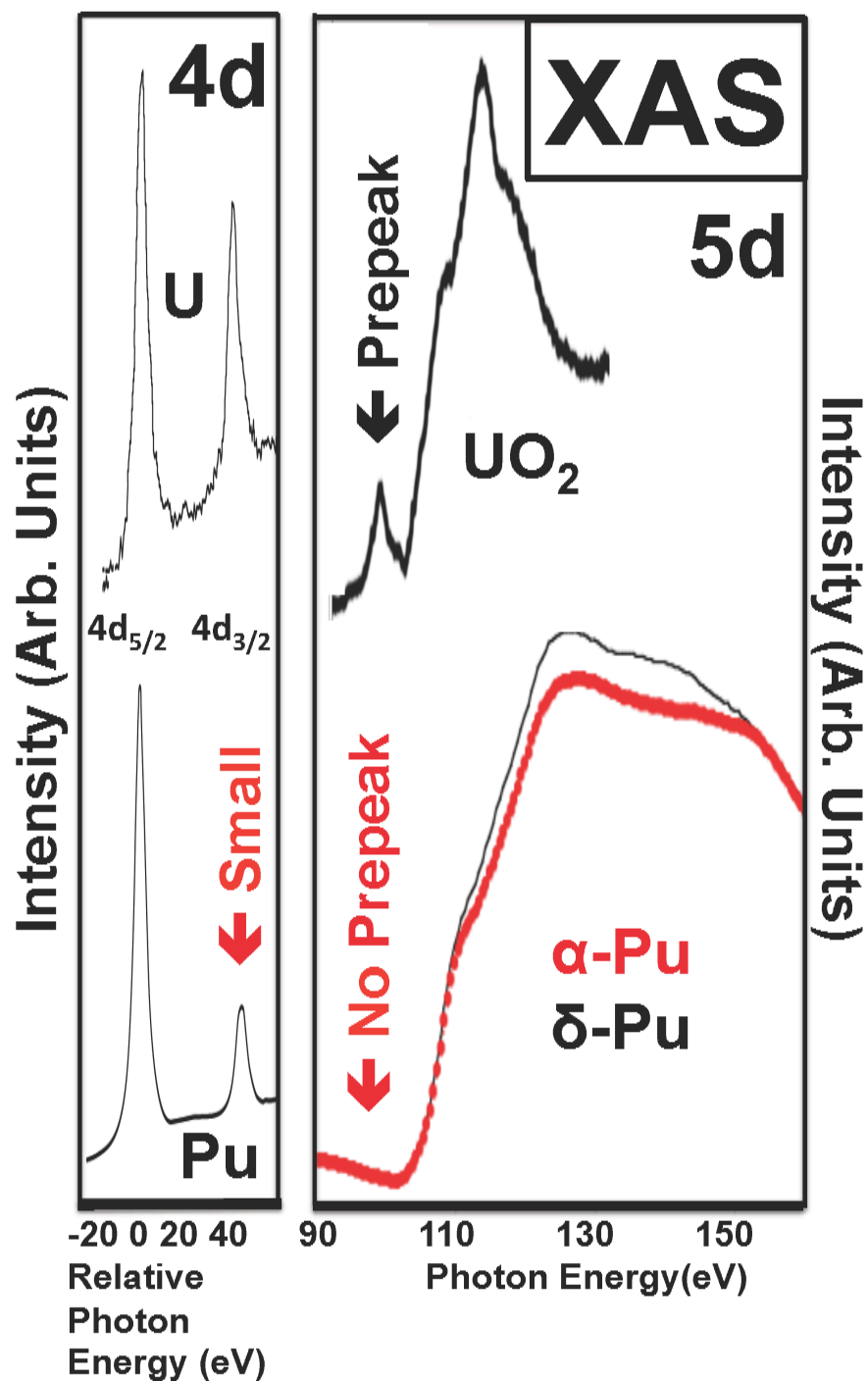

Figure 2

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds
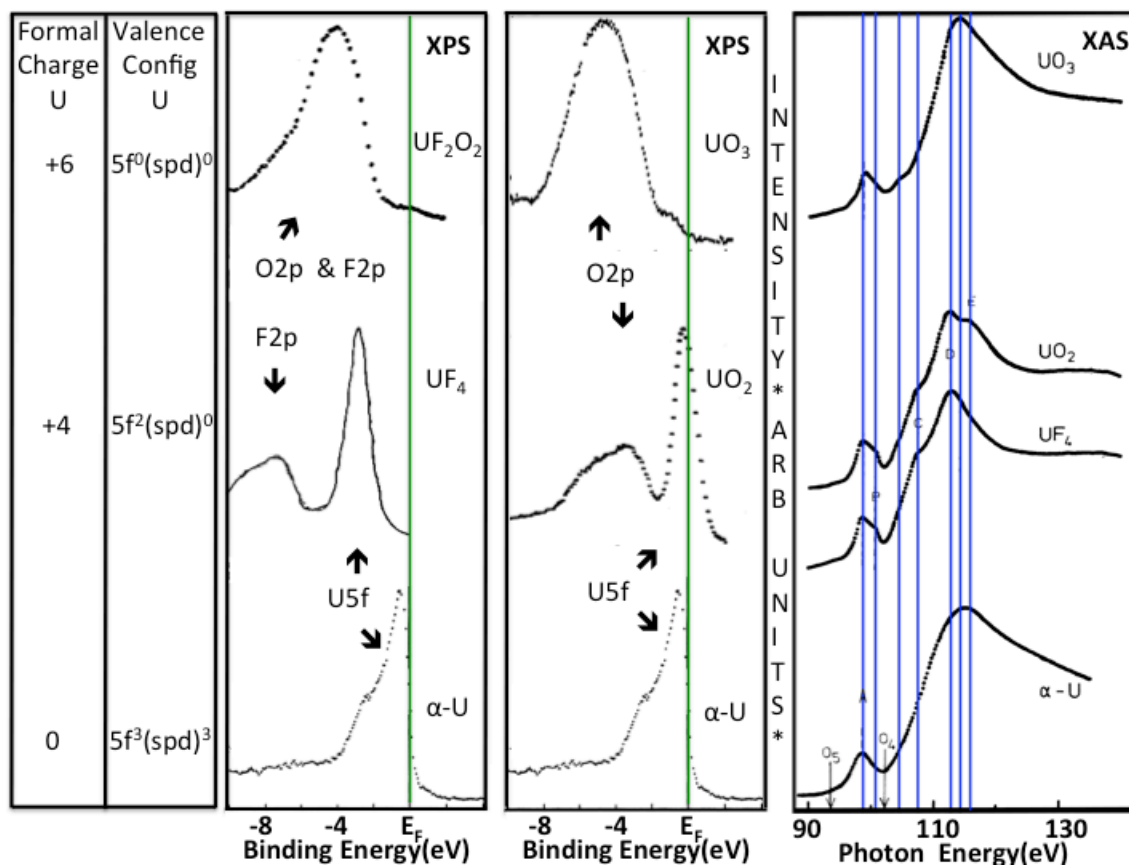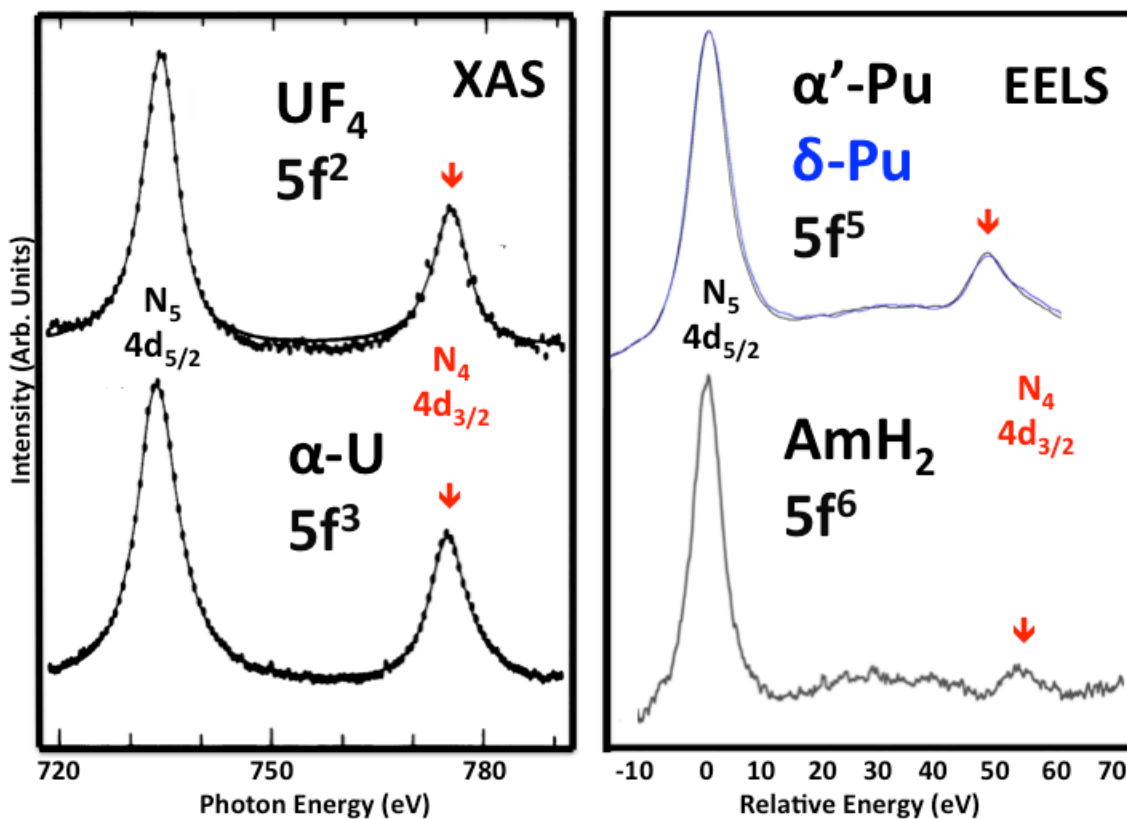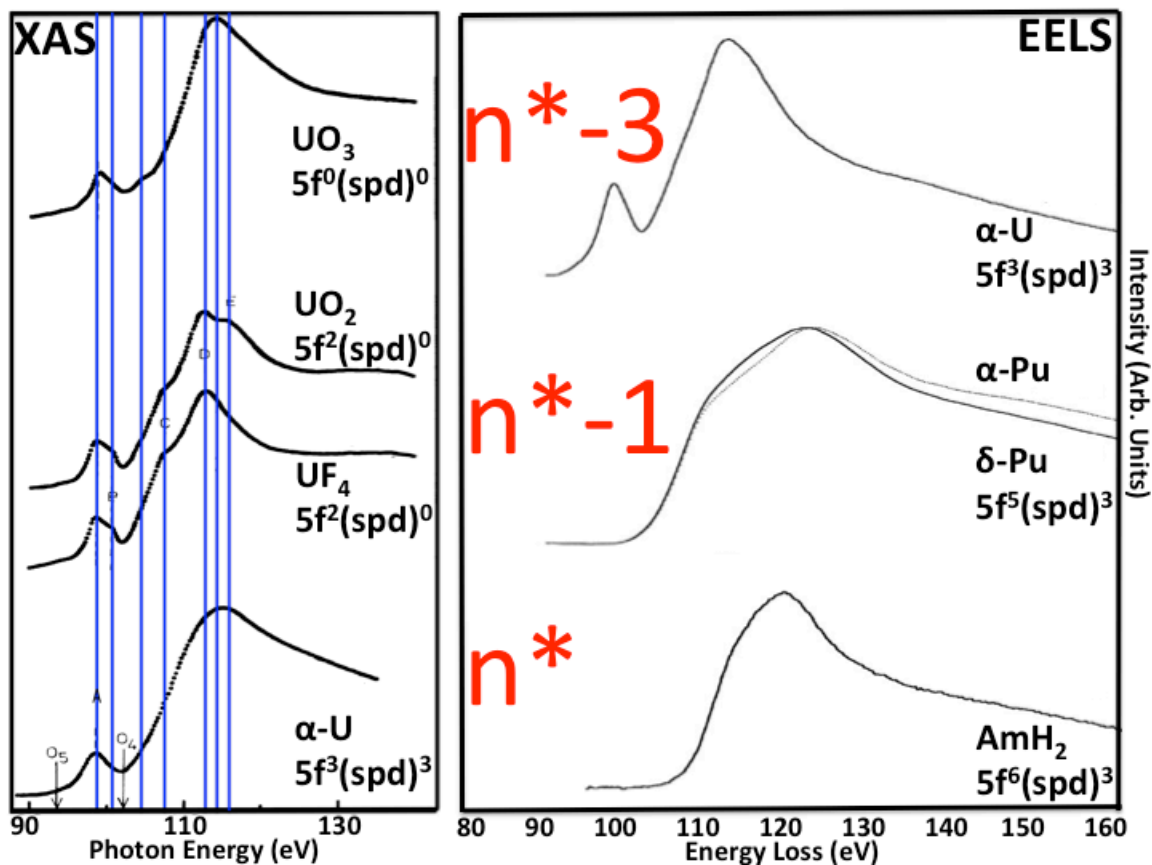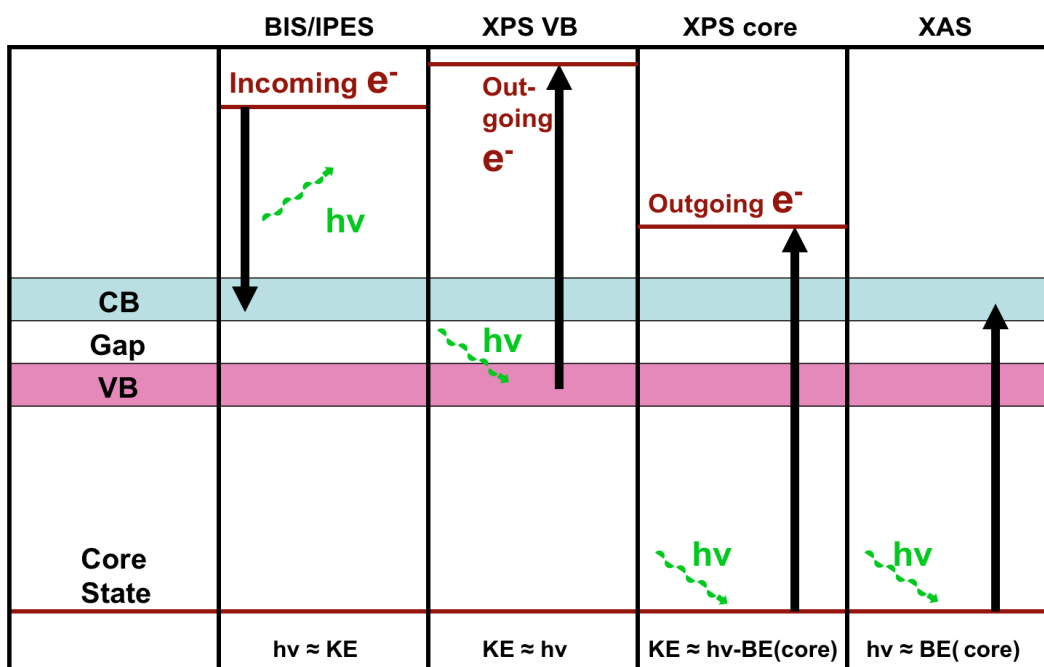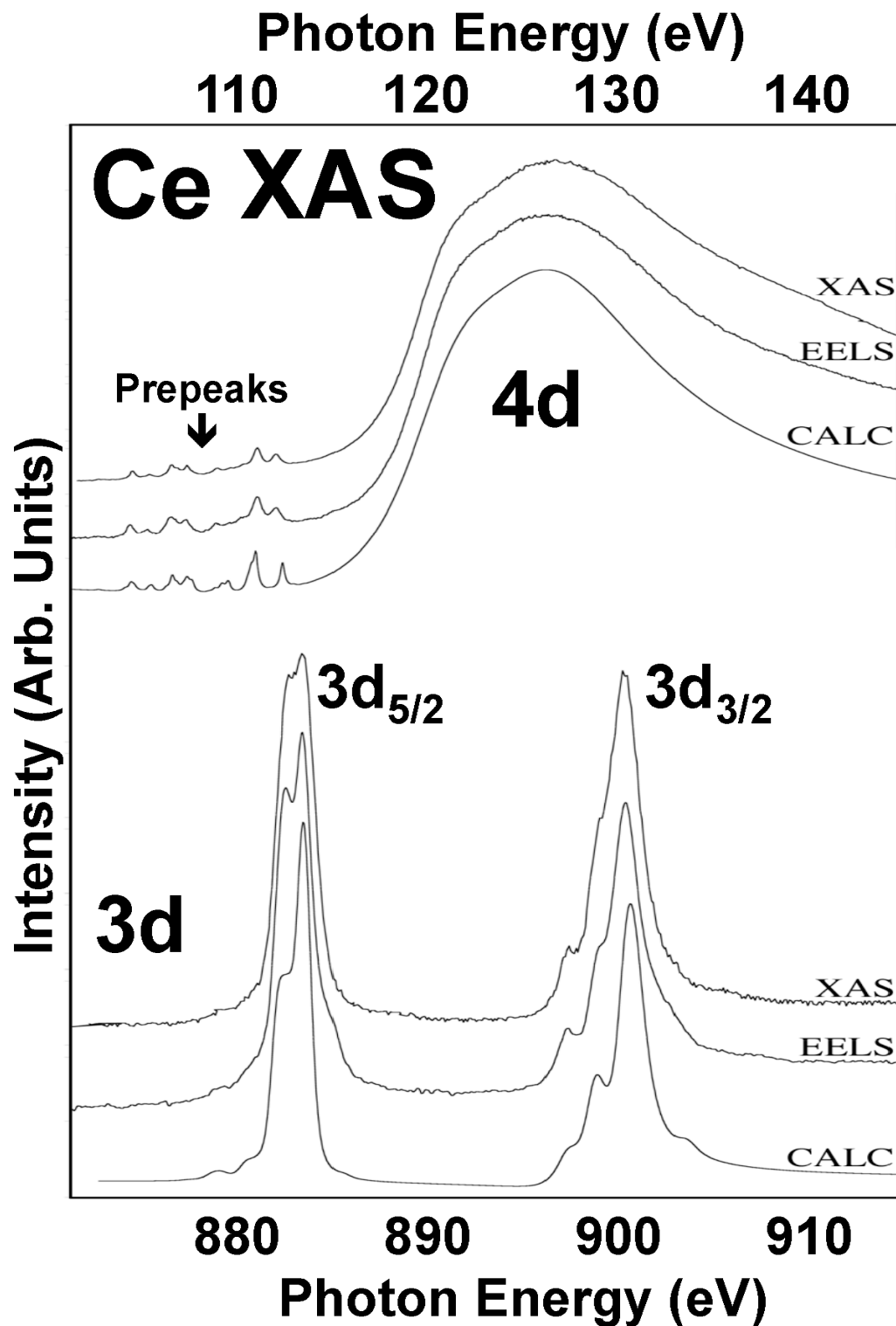

Figure 3

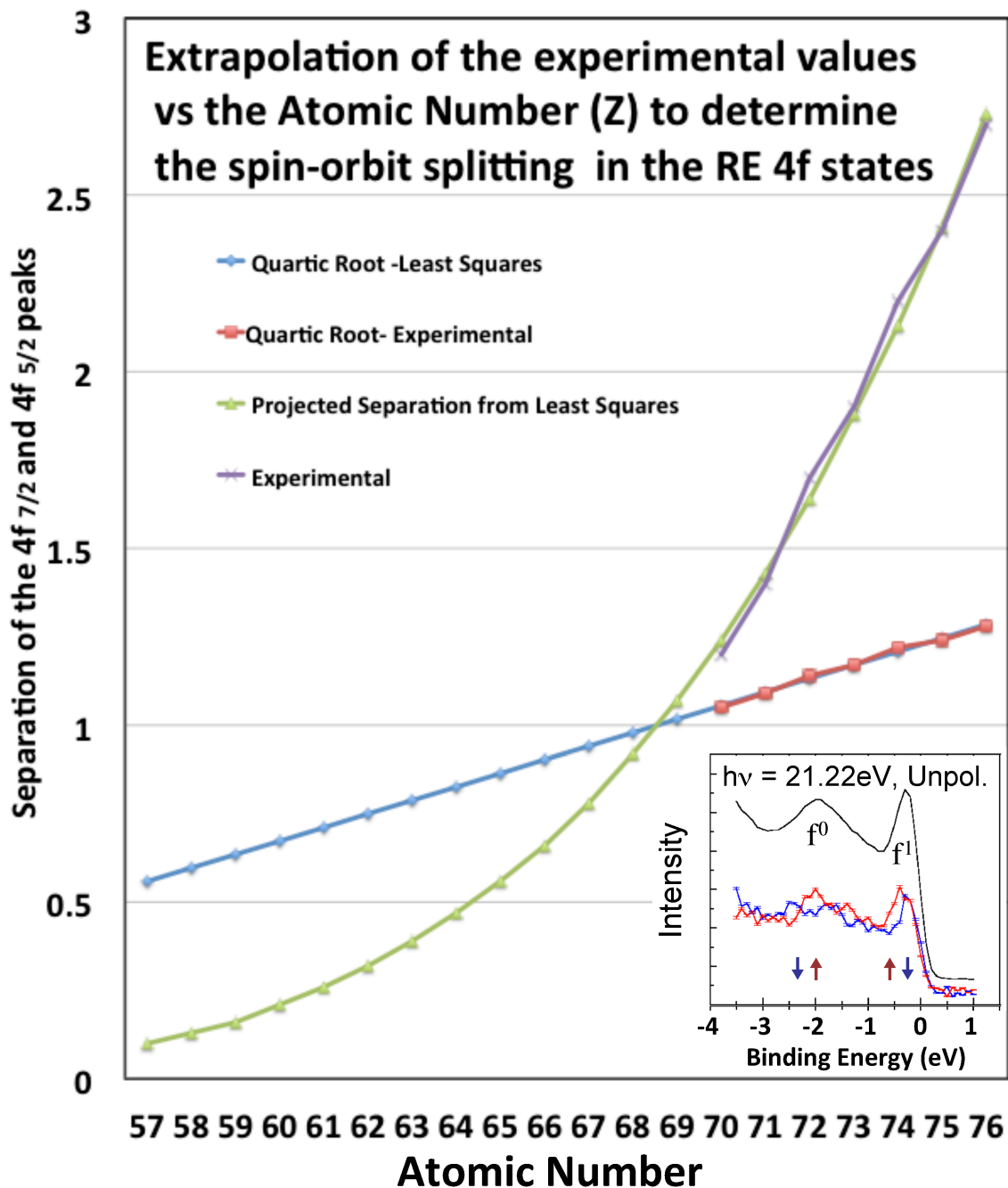# The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Figure 4

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Figure 5

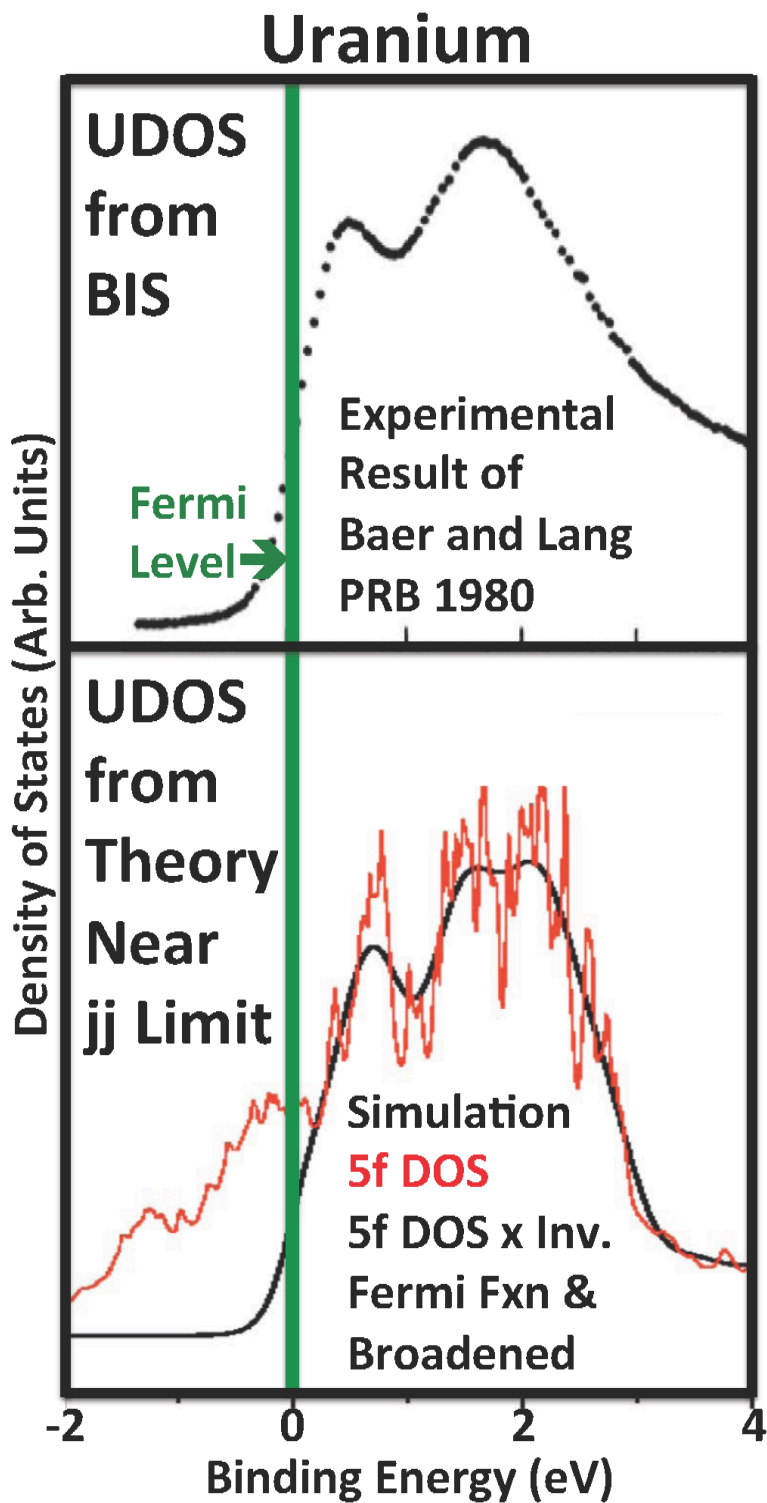# The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

BIS/IPES	XPS VB	XPS core	XAS
hv ≈ KE	KE ≈ hv	KE ≈ hv-BE(core)	hv ≈ BE(core)

Figure 6

Figure 7

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Figure 8

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Figure 9

The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds
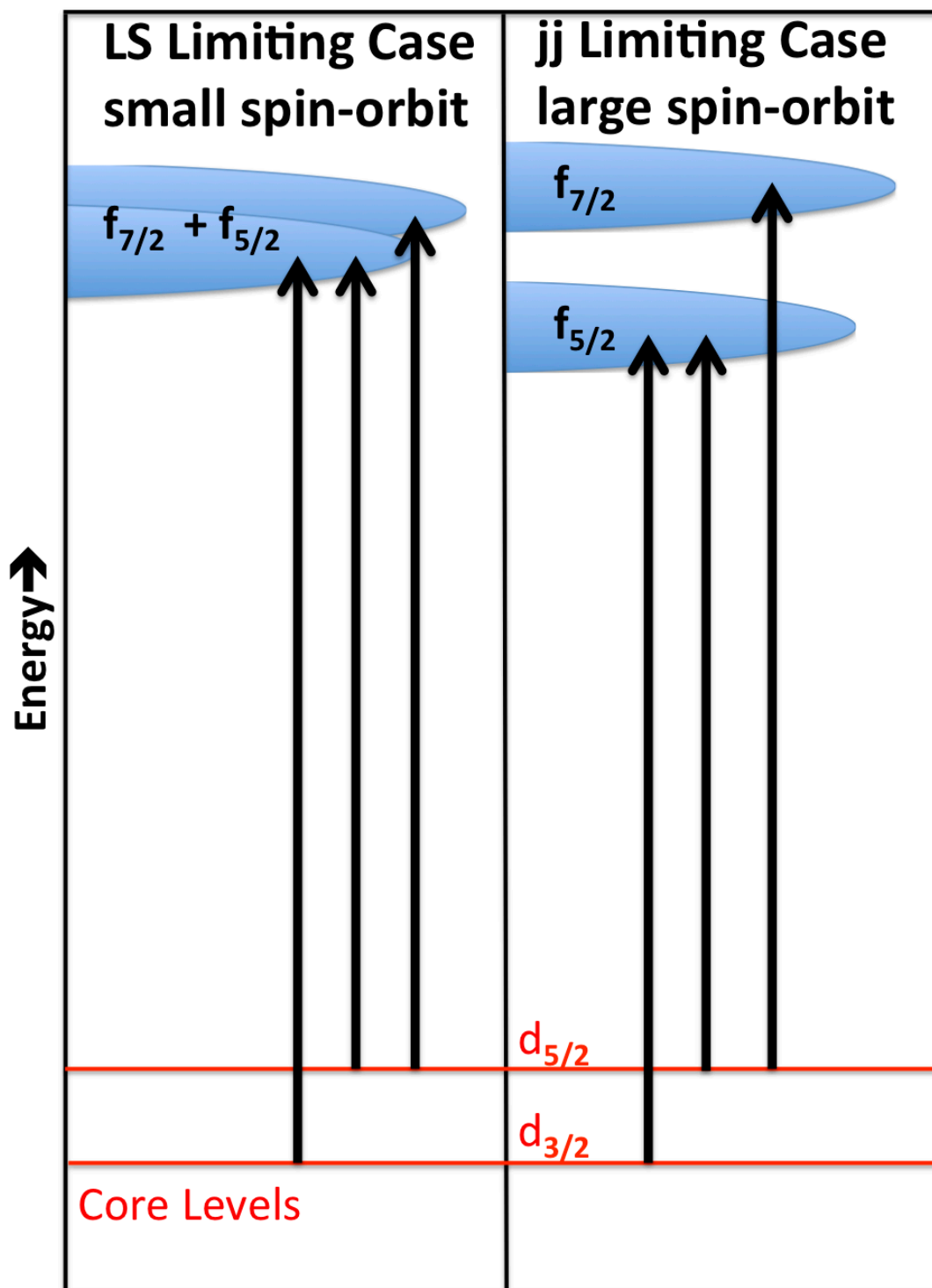

Figure 10

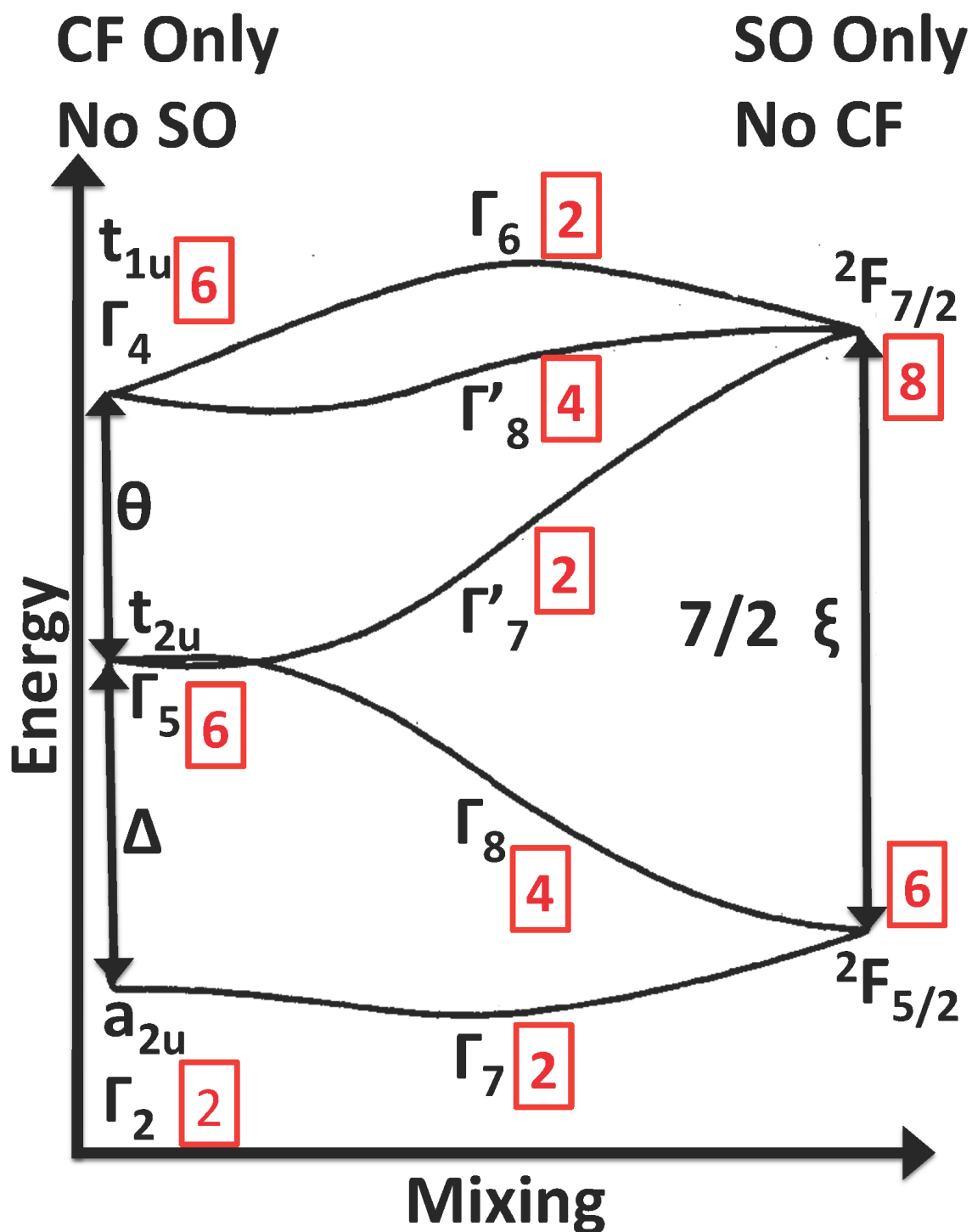# The absence of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds

Figure 11